

- 1 -

FLAME-RETARDANT POLYACETAL RESIN COMPOSITION

BACKGROUND OF THE INVENTION

The present invention relates to a polyacetal resin composition with excellent flame retardancy, more particularly to a flame-retardant polyacetal resin composition having excellent thermal stability and mechanical properties.

Polyacetal resins are used in a wide sphere of industrial products, most typically automobile and OA equipment parts, as an engineering resin with a good balance of mechanical properties and excellent moldability. However, since polyacetal resins are combustible, their use is limited in applications where flame retardancy is required. So, presently, other types of resins provided with flame retardancy are used for such applications.

Various methods have been proposed for affording flame retardancy to polyacetal resins.

For example, JP-B-43-22671 proposes the addition of ammonium phosphate to polyacetal resins, and JP-B-53-31899 discloses a method in which guanidine phosphate, melamine and ammonium polymetaphosphate are added to polyacetal resins. Further, JP-A-9-324105 teaches the incorporation of ammonium polyphosphate having a particle size of 30 μ m or less either singly or with melamine in polyacetal resins. These methods,

however, although capable of providing required flame retardancy to polyacetal resins, have the problem that the innate properties of polyacetal resins might be impaired greatly because of high loadings of the said
5 additive materials.

Further, an idea of adding red phosphorus and a triazine-based compound to polyacetal resins to provide flame retardancy thereto is disclosed in JP-A-48-7044 and JP-B-55-35421. However, in this case, too,
10 it is necessary to add a triazine-based compound such as melamine, guanidine phosphate or cyanoguanidine in a large quantity for obtaining satisfactory flame retardancy, and especially when melamine is used in bulk, there arise such problems as bleeding and mold
15 deposition. JP-A-55-84348 proposes a polyacetal resin composition improved in flame retardancy by the combined use of red phosphorus and a molybdenum compound, but this composition is unsatisfactory in thermal stability and moldability.

20 On the other hand, incorporation of phenol resins or polycarbonate resins in polyacetal resins has been known in the art. For instance, JP-B-49-42662 teaches the addition of a phenol resin to polyacetal resins as an antioxidant. Also, JP-A-6-248163, JP-A-6-
25 329873, JP-A-7-11101 and JP-A-7-292186 disclose methods featuring the addition of a phenol resin to a composition comprising a polyacetal resin and a polycarbonate, polystyrene, aliphatic polyether or

09862726 052304

aromatic polyether for improving the affinity and dispersibility of the polyacetal resin and thereby improving the mechanical properties and molding shrinkage of the composition. No disclosure has ever
5 been made, however, regarding the improvement of flame retardancy by the incorporation of a phenol resin and/or a polycarbonate resin in polyacetal resins.

As viewed above, it is very difficult on account of their inherent characteristics to provide
10 flame retardancy to polyacetal resins, and there is yet available no polyacetal resin composition which is possessed of both excellent innate properties of polyacetal resins and high flame retardancy.

SUMMARY OF THE INVENTION

15 The present invention is designed to provide a polyacetal resin composition which can be used even in the fields where the use of polyacetal resins has been limited because of their poor flame retardancy, by affording flame retardancy to polyacetal resins while
20 maintaining their excellent innate properties.

In the course of research conceiving flame-retardant polyacetal resins, the present inventors found that it is possible to make the polyacetal resins flame-retardant without vitiating their innate
25 properties by incorporating red phosphorus, a phenol resin and/or a polycarbonate resin and a thermal stabilizer in polyacetal resins, and completed the

0862726-052301

present invention on the basis of this finding.

[1] A flame-retardant polyacetal resin

5 composition comprising (A) 60 to 90% by weight of a polyacetal resin, (B) 1 to 30% by weight of red phosphorus, (C) 1 to 40% by weight of at least one resin selected from the group consisting of phenol resins and polycarbonate resins, and (D) 0.1 to 5% by

10 weight of a metal salt of a fatty acid as a thermal stabilizer.

[2] A resin composition set out in [1] above, wherein the red phosphorus is coated with an inorganic material and/or a resin.

15 [3] A resin composition set out in [1] or [2] above, wherein the red phosphorus has an average particle size of 0.1 to 100 μm .

[4] A resin composition set out in any one of [1] to [3] above, wherein the amount of red phosphorus in

20 the whole composition is 5 to 15% by weight.

[5] A resin composition set out in any one of [1] to [4] above, wherein the component (C) is a novolak phenol resin having a weight-average molecular weight of 500 to 10,000.

25 [6] A resin composition set out in any one of [1] to [5] above, wherein the component (C) is a phenol resin modified with paraxylylene or alkylbenzene.

[7] A resin composition set out in any one of [1]

to [6] above, wherein the component (C) is a phenol resin containing 5% by weight or less of unreacted phenol.

[8] A resin composition set out in any one of [1] to [7] above, wherein the metal salt (D) is at least one substance selected from the group consisting of alkaline metal salt of a fatty acid and an alkaline earth metal salt of a fatty acid.

[9] A resin composition set out in [8] above, wherein the metal salt (D) is a lithium salt of a fatty acid.

[10] A resin composition set out in [9] above, wherein the lithium salt is lithium stearate.

[11] A resin composition set out in any one of [1] to [10] above further comprising 5% by weight or less of (E) a silicon-based lubricant.

DETAILED DESCRIPTION OF THE INVENTION

A detailed description of the present invention follows.

20 The polyacetal resins usable as the component (A) in the present invention are not specified; it is possible to use, for instance, homopolymers obtained by homopolymerizing the monomers of formaldehyde, its trimer trioxane or its tetramer tetraoxane, with their molecular end closed with an ester or an ether; 25 copolymers containing C2-C8 oxyalkylene units obtained by copolymerizing said trioxane or tetraoxane and

08662726 "052301

coated with an inorganic material; red phosphorus coated with a resin; red phosphorus coated with an inorganic material and a resin; red phosphorus with a two-layer coating formed by first providing an
5 inorganic material coating and then providing thereon a resin coating; and red phosphorus subjected to a surface treatment with various types of oil.

As referred to herein, the inorganic material include, without limitation, a metal such as iron,
10 nickel, copper, aluminum, zinc, manganese, tin, titanium and zirconium; and a metal compound such as a metal hydroxide (aluminum hydroxide, magnesium hydroxide, calcium hydroxide, zinc hydroxide, titanium hydroxide, etc.) and a metal oxide (aluminum oxide,
15 magnesium oxide, zinc oxide, titanium oxide, zirconium oxide, copper oxide, iron oxide, molybdenum oxide, tungsten oxide, manganese oxide, tin oxide, etc.). As coating and stabilization methods using the metal, a coating with the metal or its alloy by an electroless
20 plating method and a formation of a metal phosphorus composition on the surface of red phosphorus by treating red phosphorus with a metal salt (aluminum, magnesium, zinc, titanium, copper, silver, iron or nickel salt) solution may be mentioned.

25 The resin which can be employed is, for example, a therosetting resin or a thermoplastic resin. Typical examples of the thermosetting resins include phenol resins, melamine resins, urea resins, alkyd

09862726-052301

resins, unsaturated polyester resins, epoxy resins, silicone resins and the like, and typical examples of the thermoplastic resins include polyester resins, polyamide resins, acrylic resins, olefin resins and the like.

In the present invention, stabilized red phosphorus coated with an inorganic material and/or a resin or stabilized red phosphorus having a two-layer coating of an inorganic material and a resin is preferably used, more preferably stabilized red phosphorus coated with a metal hydroxide such as magnesium hydroxide, aluminum hydroxide, zinc hydroxide or titanium hydroxide and/or a resin or stabilized red phosphorus having a two-layer coating of a metal hydroxide such as magnesium hydroxide, aluminum hydroxide, zinc hydroxide or titanium hydroxide and a resin.

Examples of such surface-treated red phosphorus are Novared 120, Novaexcel 140 and Novaexcel F5 (trade names) commercially available from Rin Kagaku Kogyo KK.

The particle size of red phosphorus used in the present invention is not specifically defined; no problem arises if its particle size is 200 μm or less, which is normal size, but it is preferable to use red phosphorus with a particle size of 0.1 to 100 μm , more preferably 1 to 50 μm . For the determination of particle size, for instance a method can be used in

00002726 052301

hydroxyphenyl)sulfone. Homopolymers of these divalent phenols and copolymers of two or more types of divalent phenols are also usable.

As the polycarbonate resin in the present
5 invention, it is possible to use the copolymers of polycarbonates such as polyester carbonate and the branched polycarbonate resins.

Examples of such polycarbonate resins are the commercial products Panlite L-1225 (trade name) by
10 Teijin Kasei Co., Ltd., and Iupilon S2000, S2000R, S3000 and S3000R (trade name) by Mitsubishi Engineering Plastics Co., Ltd.

The amount of the component (C) in the whole composition is 1 to 40% by weight, preferably 5 to 20%
15 by weight. If the amount of the component (C) is less than 1% by weight, it is impossible to obtain the desired flame retardancy, and if its amount exceeds 40% by weight, although satisfactory flame retardancy can be obtained, the innate mechanical properties of the
20 polyacetal resins are impaired.

The metal salt of a fatty acid used as component (D) (thermal stabilizer) in the present invention is at least one compound selected from the group consisting of an alkaline metal salt of a fatty
25 acid and an alkaline earth metal salt of a fatty acid.

Examples of the alkaline metal fatty acid salt and the alkaline earth metal salt are calcium dimyristate, calcium dipalmitate, calcium

05652726 "052301

diheptadecylate, calcium distearate, calcium
(myristate-palmitate), calcium (myristate-stearate),
calcium (palmitate-stearate), lithium myristate,
lithium palmitate, lithium heptadecylate and lithium
5 stearate. Of these compounds, a lithium salt of a
fatty acid such as lithium palmitate and lithium
stearate; and a calcium salt of a fatty acid such as
calcium distearate are preferred, and lithium stearate
are especially preferred. These compounds may be used
10 either singly or as a mixture of two or more of them.

The amount of the thermal stabilizer in the
whole composition is 0.1 to 5% by weight, preferably
0.15 to 3% by weight. If the amount of the thermal
stabilizer is less than 0.1% by weight, the desired
15 thermal stability may not be obtained due to the
influence of phosphoric acid generated from the
decomposition of red phosphorus or unreacted phenol in
the phenol resin. If the amount of the thermal
stabilizer exceeds 5% by weight, flame retardancy is
20 impaired.

The composition according to the present
invention may further contain (E) a silicon-based
lubricant in addition to the said components (A) to
(D). The silicon-based lubricant used in the present
25 invention may be optionally selected from the known
silicon compounds and their modified products. These
silicon compounds may be used by combining two or more
of them. Further, for the sake of convenience of

00862726-052301

pellets are mixed with a phenol resin and/or a polycarbonate resin, a thermal stabilizer, etc., the mixture being then extruded and pelletized.

Red phosphorus has the property that it is easily ignited when an impact or frictional force is given thereto, so that a great deal of care is required for handling of powdery red phosphorus. For facilitating handling of red phosphorus, it is preferred to form masterbatch pellets of red phosphorus with a polyacetal resin as mentioned above. This method can greatly facilitate the handling of powdery red phosphorus.

The polyacetal resin composition of the present invention is provided with flame retardancy while maintaining the excellent innate properties of polyacetal resins, so that it can be applied to the fields where its use has been considered difficult, such as the fields of automobile parts and OA equipment parts.

20 DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention will be further illustrated by showing the examples thereof. The component materials used in the Examples and the Comparative Examples are as described below.

25 (A) Polyacetal resin

TENAC C (trade name) 4520 produced by Asahi Kasei Kogyo K.K.; MI = 10 g/10 min

0062726*052301

(B) Red phosphorus

(B1): Novaexcel 140 produced by Rin Kagaku Kogyo KK;
an inorganic material/resin two-layer coating;
average particle size = 40 μ m

5 (B2): Novared 120 produced by Rin Kagaku Kogyo KK;
an inorganic material/resin mixture coating;
average particle size = 30 μ m

(C) Phenol and polycarbonate resins

Phenol resins

10 (C1): PR-50731 produced by Sumitomo Durez Co., Ltd.;
Novolak type, weight-average molecular weight:
7,600;

unreacted phenol = 2%

(C2): R-54537 produced by Sumitomo Durez Co., Ltd.;

15 Novolak type, weight-average molecular weight:
3,400;

unreacted phenol < 2%; 65% modified with
alkylbenzene

Polycarbonate resin

20 (C2): Panlite L1225 produced by Teijin Kasei Co.,
Ltd.

(D) Thermal stabilizers

(D1): lithium stearate produced by Nippon Yushi KK

(D2): melamine produced by Nissan Chemical Co., Ltd.;

25 average particle size = 1 micron

(D3): nylon 12 (Diamid L-1700) produced by Daicel
Chemical Industries, Ltd.

(E) Silicon-based lubricant

00862726-052301

SP-350, master pellets produced by Dow Corning Asia, Ltd.

The evaluation of flame retardancy, properties and thermal stability in the following Examples and

5 Comparative Examples was made by the methods described below.

(1) Flame retardancy

Five $127 \times 12.7 \times 3$ mm test pieces were left in an atmosphere of 23°C and 50% RH for 2 days and then
10 brought into contact with the flames according to the UL Flame Resistance Test Standards (UL 94 ranking: HB, V-2, V-1, V-0), and the ranking of the test pieces by the same Standards was made based on the combustion time after each of 2 times of contact with the flames
15 and the total combustion time after 10 times of contact with the flames.

(2) Flexural modulus

The test pieces were made using an injection molding machine IS-100E (Toshiba Corp.) under the
20 following conditions: cylinder temperature = 200°C ; injection pressure = 6 MPa; injection time = 25 seconds; cooling time = 15 seconds; mold temperature = 70°C , and their flexural modulus was determined according to ASTM-D790.

25 (3) Izod impact strength

The test pieces were made using the above-mentioned injection molding machine (Toshiba IS-100E) under the following conditions: cylinder temperature =

00002726 000004

200°C; injection pressure = 6 MPa; injection time = 25 seconds; cooling time = 15 seconds; mold temperature = 70°C, and they were notched and subjected to an Izod impact test according to ASTM-D256.

5 (4) Thermal stability

Each specimen was melted by heating at 230°C in a stream of nitrogen and the formaldehyde generated in the period of 30 minutes was absorbed into a sodium sulfite solution and titrated with a sulfuric acid
10 solution.

Example 1

68% by weight of polyacetal resin (A), 30% by weight of red phosphorus (B1) and 2% by weight of thermal stabilizer (D1) were blended and pelletized by
15 a double-screw extruder (PCM-30 mfd. by Ikegai Iron Works, Ltd.) at 190°C to obtain a 30% red phosphorus masterbatch. In this masterbatch, polyacetal resin (A), phenol resin (C1) and thermal stabilizer (D1) were blended so that the component contents in the whole
20 composition would become 83% by weight (A), 10% by weight (B1), 6% by weight (C1) and 1% by weight (D1), respectively, and the blend was pelletized by the double-screw extruder (Ikegai Iron Works PCM-30) at 190°C. The obtained pellets were molded into the test
25 pieces and these test pieces were left in a room controlled at 23°C and 50% RH for 2 days and then subjected to the determinations of flame retardancy,

0062726 "052301

flexural modulus and Izod impact strength. Thermal stability of the pellets was also determined. Evaluation results are shown in Table 1.

Example 2

5 83% by weight of polyacetal resin (A), 10% by weight of red phosphorus (B1), 6% by weight of phenol resin (C1) and 1% by weight of thermal stabilizer (D1) were blended and pelletized by the double-screw extruder (Ikegai Iron Works PCM-30) at 190°C. The
10 obtained pellets were molded into test pieces, and these test pieces were left in a room controlled at 23°C and 50% RH for 2 days and then subjected to the determinations of flame retardancy, flexural modulus and Izod impact strength. Evaluation results are shown
15 in Table 1.

Examples 3 to 7

Test pieces were made in the same way as in Example 1 except that the type and amount of the phenol resin, flame retardant and thermal stabilizer were
20 changed as shown in Table 1, and they were evaluated as in Example 1. Evaluation results are shown in Table 1.

Example 8

Test pieces were made in the same way as in Example 4 except that 2% by weight of a silicon-based
25 lubricant (E) was further added to the master batch,

00000726 052301

and they were evaluated as in Example 1. Results are shown in Table 1.

Comparative Examples 1 to 15

Test pieces were made in the same way as in Example 1 except that the type and composition of the phenol resin, flame retardant and thermal stabilizer were changed as shown in Table 2, and they were evaluated as in Example 1. Results are shown in Table 2.

Table 1

	POLY- ACETAL RESIN	RED PHOSPHORUS		PHENOL RESIN (C1, C2) POLYCARBONATE RESIN (C3)	
	wt%	TYPE	wt%	TYPE	wt%
EXAMPLE 1	83.0	(B1)	10	(C1)	6
EXAMPLE 2	83.0	(B1)	10	(C1)	6
EXAMPLE 3	83.0	(B2)	10	(C1)	6
EXAMPLE 4	83.0	(B1)	10	(C2)	6
EXAMPLE 5	79.0	(B1)	10	(C3)	10
EXAMPLE 6	76.0	(B1)	10	(C1)/(C3)	5/8
EXAMPLE 7	76.0	(B1)	10	(C2)/(C3)	5/8
EXAMPLE 8	81.0	(B1)	10	(C2) +(E)LUBRICANT	6 +2

0862726-052304

THERMAL STABILIZER		FLEXURAL MODULUS	IZOD IMPACT STRENGTH	THERMAL STABILITY	UL94 RANKING
TYPE	wt%	GPa	J/m	ppm	-
(D1)	1	2.57	35	200	V-1
(D1)	1	2.53	34	150	V-1
(D1)	1	2.46	34	240	V-1
(D1)	1	2.46	35	180	V-1
(D1)	1	2.50	35	170	V-1
(D1)	1	2.45	33	210	V-1
(D1)	1	2.51	35	170	V-1
(D1)	1	2.45	34	200	V-1

Table 2

	POLY- ACETAL RESIN	RED PHOSPHORUS		PHENOL RESIN (C1, C2) POLYCARBONATE RESIN (C3)	
	wt%	TYPE	wt%	TYPE	wt%
COMP. EXAMPLE 1	99	-	0	-	0
COMP. EXAMPLE 2	89.9	(B1)	10	-	0
COMP. EXAMPLE 3	79.0	(B1)	20	-	0
COMP. EXAMPLE 4	89.0	-	0	(C1)	10
COMP. EXAMPLE 5	89.0	-	0	(C2)	10
COMP. EXAMPLE 6	89.0	-	0.1	(C3)	10
COMP. EXAMPLE 7	88.9	(B1)	0.1	(C2)	10
COMP. EXAMPLE 8	88.9	(B1)	40	(C3)	10
COMP. EXAMPLE 9	53.0	(B1)	40	(C2)	6
COMP. EXAMPLE 10	53.0	(B1)	15	(C3)	6
COMP. EXAMPLE 11	83.5	(B1)	15	(C2)	0.5
COMP. EXAMPLE 12	83.5	(B1)	15	(C3)	0.5
COMP. EXAMPLE 13	39.0	(B1)	15	(C2)	45
COMP. EXAMPLE 14	39.0	(B1)	15	(C3)	45
COMP. EXAMPLE 15	84.0	(B1)	10	(C1)	6

08662726-052301

Table 2 (Cont'd)

THERMAL STABILIZER		FLEXURAL MODULUS	IZOD IMPACT STRENGTH	THERMAL STABILITY	UL94
TYPE	wt%	GPa	J/m	ppm	RANKING
(D1)	1	2.65	60	100	HB
(D1)	0.05	2.83	37	2300	HB
(D1)	1	3.25	21	490	HB
(D1)	1	2.05	55	380	HB
(D1)	1	2.10	55	290	HB
(D1)	1	2.60	36	280	HB
(D1)	1	2.02	55	220	HB
(D1)	1	2.65	35	220	HB
(D1)	1	2.75	17	1510	V-1
(D1)	1	2.85	17	1350	V-1
(D1)	1	2.75	43	300	HB
(D1)	1	2.72	45	280	HB
(D1)	1	1.21	16	370	V-1
(D1)	1	2.28	16	230	V-1
(D1)	0	2.56	35	780	V-1

00662726 062301